



## In situ study by XAS of the sulfidation of industrial catalysts: the Pt and PtRe/Al<sub>2</sub>O<sub>3</sub> systems

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### Abstract

Extended X-ray absorption fine structure (EXAFS) spectroscopy has been used to follow the structural evolution of the monometallic Pt/Al<sub>2</sub>O<sub>3</sub> and the bimetallic Pt–Re/Al<sub>2</sub>O<sub>3</sub> systems during reduction and sulfidation treatments. After sulfidation a second reduction has been performed in order to study the elimination of reversibly adsorbed sulfur. For the monometallic system, starting from the reduced state, the number of platinum–platinum bonds decreases significantly from 4.5 to 1.5 after sulfidation and a second reduction. In addition, a significant amount of sulfur is measured around platinum atoms (3 sulfur atoms per platinum atom). On the contrary, for the bimetallic platinum–rhenium system, the number of sulfur atoms in the vicinity of platinum atoms is smaller (1 sulfur atom per platinum atom) with no major change for the number of platinum–platinum bonds. Simultaneous measurements at the rhenium absorption edge show that the sulfur atoms are preferentially fixed by the rhenium atoms (2 sulfur atoms per rhenium atom). From these quantitative results, a structural model for both the monometallic and the bimetallic systems is proposed to describe the different behaviors. © 1997 Elsevier Science B.V.

**Keywords:** Platinum; Rhenium; Sulfur; XAS; Sulfidation

### 1. Introduction

During the 1950 and 1960s, platinum supported catalysts dominated catalytic reforming. Platinum is well known to be highly active for hydrogenation, the role of the support being to accelerate acid catalyzed reactions such as isomerization and cyclization. Then, during the 1970s, the concept of bimetallic catalysts emerged and the Pt–Re catalyst [1] as well as the Pt–Ir catalyst [2,3] have largely replaced the older Pt/Al<sub>2</sub>O<sub>3</sub> catalysts in reforming units. In order to improve the

performance of the bimetallic PtRe/Al<sub>2</sub>O<sub>3</sub> from a selectivity and a stability point of view, this system is presulfided [4–6] during start up to decrease the high hydrogenolysis activity of the fresh catalyst.

In this work, we report a comparison between monometallic platinum and the bimetallic platinum–rhenium, both deposited on alumina, aimed at understanding the role of the second metal during the sequence of reduction and sulfidation. A second reduction was carried out to study the reversibility sulfur fixation. We begin by a description of the monometallic sample at each step. The platinum–rhenium bimetallic sample is then studied and parti-

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cular attention is paid to the sulfidation step. The backscattering amplitudes and phase-shift functions for chlorine and sulfur are very similar ( $Z=17$  and  $16$ , respectively) and, in order to distinguish between chlorine and sulfur in the vicinity of the metal atoms, a non-chlorinated bimetallic has been studied under the same conditions as a chlorinated bimetallic one.

## 2. Experimental

### 2.1. Catalysts

The samples are highly dispersed platinum and platinum–rhenium clusters deposited on  $\gamma$ -alumina extrudates (BET surface area  $240 \text{ m}^2/\text{g}$ ). For platinum–rhenium, we used successive impregnation of  $\text{NH}_4\text{ReO}_4$  first, followed by  $\text{H}_2\text{PtCl}_6$  [7,8]. Table 1 reports the composition of the different catalysts, the metal and halogen contents being determined by X-ray fluorescence.

The non-chlorinated platinum–rhenium on  $\gamma_c$  alumina catalyst was obtained by successive washing with ammonia until wt% of  $\text{Cl} < 0.1$ . During the treatment, the catalysts were reduced under flowing hydrogen at  $723 \text{ K}$  for  $2 \text{ h}$ , and then sulfided under a gaseous mixture of  $1\% \text{ H}_2\text{S}$  in  $\text{H}_2$  at  $723 \text{ K}$  for  $2 \text{ h}$ . After the sulfidation treatment, the catalysts were again reduced with  $\text{H}_2$  at  $723 \text{ K}$  to eliminate reversibly adsorbed sulfur.

The extended X-ray absorption fine structure (EXAFS) experiments required only small quantities

of the catalysts ( $0.2 \text{ g}$ ) and gas flow rates were high (over  $10\,000 \text{ cm}^3/\text{g}$  per hour). Under these conditions control experiments increasing the treatment times showed that  $2 \text{ h}$  was sufficient to complete the reactions [9].

### 2.2. EXAFS experiments

EXAFS spectra were collected at the LURE synchrotron facility in Orsay using the synchrotron radiation from the DCI storage ring running at  $1.85 \text{ GeV}$  with an average current of  $300 \text{ mA}$ . The spectra were measured at the  $L_{III}$  edge of platinum for the monometallic and at both the platinum and rhenium  $L_{III}$  edges for the bimetallic samples. The EXAFS data were obtained on the EXAFS IV station with a double crystal  $\text{Si}(111)$  monochromator, in the transmission mode and using two ionization chambers as detectors. Calibration of the experiment was made with reference metal foils.

The catalysts were in powder form screened to  $100\text{--}200 \text{ mm}$ . They were placed in a special furnace for in situ sulfidation treatment with entrance and exit windows of boron nitride transparent to the X-ray beam. EXAFS spectra were measured during in situ treatment, cooling the catalysts to room temperature after a stabilization period of  $1 \text{ h}$  for each treatment. On-line data analysis was used in order to check that the chemical reaction was proceeding.

### 2.3. Analytical procedure

The EXAFS formalism and analytical procedure used is a standard one. Fourier transforms of the  $k^3$  weighted EXAFS functions were obtained using a Hanning type window ranging from  $40$  to  $400 \text{ eV}$  after the platinum edge and from  $40$  to  $500 \text{ eV}$  after the rhenium edge. The  $k^3$  weighting minimizes the effect on the Fourier transform of decreasing EXAFS signal with increasing  $k$ . A  $k^1$  weighting would increase sensitivity to low atomic number neighbors (S, O) but would severely decrease the precision for analysis of metal–metal neighbors. The inverse Fourier transforms (filtered EXAFS) were then obtained from the range  $1.0\text{--}3.2 \text{ \AA}$ . The experimental phase shifts and backscattering amplitudes were extracted from the appropriate experimental references using the same data treatment. In this work, platinum metal

Table 1  
Sample characteristics and procedures for the materials considered for the different treatments

	$\text{Pt}/\text{Al}_2\text{O}_3$	$\text{Pt-Re}/\text{Al}_2\text{O}_3$
Precursors	$\text{H}_2\text{PtCl}_6$	$\text{NH}_4\text{ReO}_4$ and $\text{H}_2\text{PtCl}_6$
Impregnation		Successive
Concentration	$1 \text{ wt\% Pt}$ , $1.2 \text{ wt\% Cl}$	$1 \text{ wt\% Pt}$ , $1 \text{ wt\% Re}$ , $1.2 \text{ wt\% Cl}$
Drying	$24 \text{ h at } 383 \text{ K}$	$24 \text{ h at } 383 \text{ K}$
Calcination	$2 \text{ h at } 803 \text{ K}$	$2 \text{ h at } 803 \text{ K}$
First reduction	$2 \text{ h at } 723 \text{ K}$	$2 \text{ h at } 723 \text{ K}$
Sulfuration	$2 \text{ h at } 723 \text{ K}$	$2 \text{ h at } 723 \text{ K}$
Second reduction	$2 \text{ h at } 723 \text{ K}$	$2 \text{ h at } 723 \text{ K}$

foil was used as a reference for the Pt–Pt interactions, PtO<sub>2</sub> for the Pt–O interactions, and H<sub>2</sub>PtCl<sub>6</sub> for Pt–Cl and Pt–S interactions. The justification for the use of the latter reference in platinum–sulfur interactions is provided by both theoretical and experimental results [10,11]. A reduced 15 wt% Re/Al<sub>2</sub>O<sub>3</sub> catalyst was used as a reference for the Re–Re interactions, NH<sub>4</sub>ReO<sub>4</sub> for the Re–O interactions, and H<sub>2</sub>PtCl<sub>6</sub> for Re–Cl and Re–S interactions. Consideration of the theoretical Pt–Cl, Pt–S, Re–Cl and Re–S backscattering amplitudes showed that the error induced by this approximation is of the order of 5% of the number of neighbors.

A two-shell least-squares fitting procedure using the single scattering EXAFS formulation was used to extract the coordination number (*N*), distance (*R*) and Debye–Waller factor (*s*). For all simulations the edge shift  $\Delta E$  was maintained at less than 4 eV. The backscattering amplitude and phase-shift functions for platinum and rhenium are very similar, (*Z*=75 and 78, respectively) so it is not possible to distinguish between them. For the platinum and rhenium L<sub>III</sub> edge of the Pt–Re/Al<sub>2</sub>O<sub>3</sub> samples, we allude to the nearest neighbors of these metals as platinum-metal or rhenium-metal (Me=Pt and/or Re) using only the Pt–Pt and Re–Re references, respectively, to obtain phase shifts and backscattering amplitudes.

### 3. Results

#### 3.1. Monometallic Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> alumina catalyst

The EXAFS functions and the modulus of the Fourier transform are shown in Fig. 1(A) and (B), respectively. The results are presented in Table 2. The

original sample presents an average platinum–oxygen coordination number of 6.2 in line with previous work [12–14]. There is some divergence in the literature as to whether chlorine is retained in the local platinum environment after calcination, but the differences may be due to variations in global chlorine content and calcination temperature.

During the hydrogen treatment, the platinum is reduced to the metallic state, with a platinum–platinum coordination number of 4.5 and an average interatomic distance of 2.72 Å. For the platinum–oxygen coordination, we measure a number of 0.4 which is negligible considering the precision of  $\pm 0.5$  for coordination numbers measured by EXAFS thus showing that the platinum particles are fully reduced. After sulfidation in flowing 1% H<sub>2</sub>S in H<sub>2</sub> at 723 K, the platinum environment is essentially formed by sulfur atoms, and the metallic particles have disappeared. A coordination number for platinum–sulfur of 2.8 at a distance of 2.32 Å was found. Finally, after a second reduction in flowing hydrogen at 723 K, the environment of platinum atoms is composed of 2.8 atoms of sulfur at 2.30 Å and 1.5 platinum atoms at 2.71 Å.

The value of  $\Delta\sigma_{\text{Pt-S}}$  is rather high, 0.09 Å. Error analysis showed that variations in the Debye–Waller factor of 0.04 Å correlated to variations in *N<sub>S</sub>* of 0.4. Thus it may be that *N<sub>S</sub>* is over estimated. However, the quality of the data fitting was severely degraded by this size of variation in  $\Delta\sigma$  and the high value is more likely to be related to disorder in the Pt–S bonds after reformation of platinum clusters.

#### 3.2. Bimetallic PtRe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-Cl catalyst

The normalized EXAFS functions obtained at the platinum L<sub>III</sub> edge for the platinum–rhenium on alu-

Table 2  
Numerical results of the analysis of Pt/Al<sub>2</sub>O<sub>3</sub> beyond the L<sub>III</sub> platinum edge

	Number of atoms	Distances (Å)	Debye–Waller factor <sup>a</sup> (Å)
Initial catalyst	<i>N<sub>O</sub></i> =6.2	<i>R<sub>Pt-O</sub></i> =2.04	$\Delta\sigma_{\text{Pt-O}}$ =0.00
First reduction H <sub>2</sub> , 723 K	<i>N<sub>O</sub></i> =0.4	<i>R<sub>Pt-O</sub></i> =2.01	$\Delta\sigma_{\text{Pt-O}}$ =0.00
	<i>N<sub>Pt</sub></i> =4.5	<i>R<sub>Pt-Pt</sub></i> =2.72	$\Delta\sigma_{\text{Pt-Pt}}$ =0.04
Sulfidation 1% H <sub>2</sub> S/H <sub>2</sub> , 723 K	<i>N<sub>S</sub></i> =2.8	<i>R<sub>Pt-S</sub></i> =2.32	$\Delta\sigma_{\text{Pt-S}}$ =0.01
Second reduction H <sub>2</sub> , 723 K	<i>N<sub>S</sub></i> =2.8	<i>R<sub>Pt-S</sub></i> =2.30	$\Delta\sigma_{\text{Pt-S}}$ =0.09
	<i>N<sub>Pt</sub></i> =1.5	<i>R<sub>Pt-Pt</sub></i> =2.71	$\Delta\sigma_{\text{Pt-Pt}}$ =0.02

<sup>a</sup> $\Delta\sigma$  is the DW factors difference between the catalyst and the reference compound.

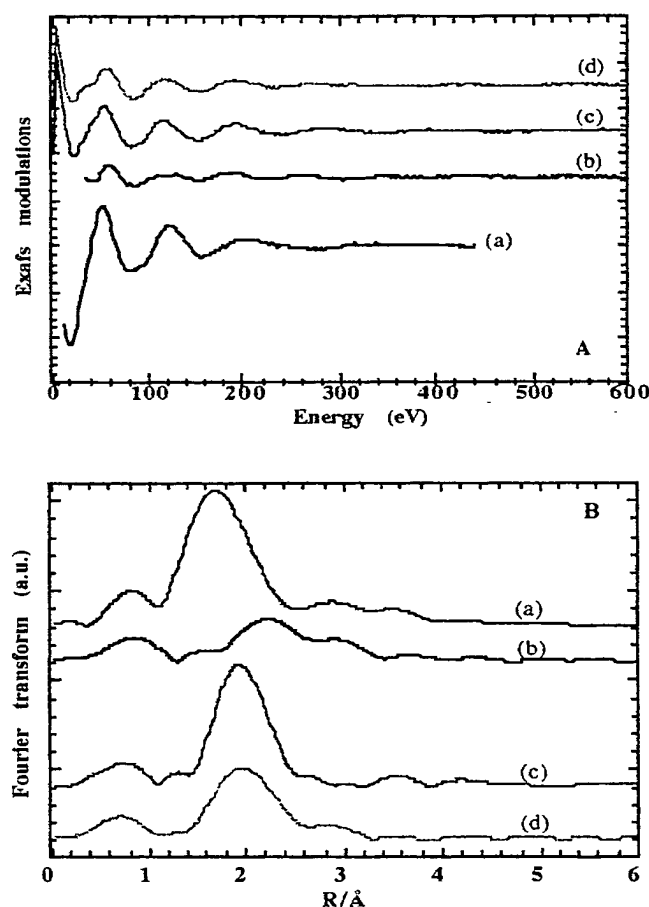


Fig. 1. EXAFS data (A) and corresponding Fourier transforms (B) for the Pt/Al<sub>2</sub>O<sub>3</sub>-Cl sample collected during the following treatments: (a) calcined; (b) H<sub>2</sub>, 723 K; (c) 1% H<sub>2</sub>S in H<sub>2</sub>, 723 K; (d) second reduction H<sub>2</sub>, 723 K.

mina sample after the different treatments are presented in Fig. 2(A) and the Fourier transforms are shown in Fig. 2(B). After inverse Fourier transform, the platinum EXAFS function was fitted using the appropriate references and the results are presented in Table 3(a). After reduction at 723 K, this catalyst presents an average platinum–metal coordination number of 3.9 at a distance of 2.71 Å. Only traces of platinum–oxygen coordination were detected. After the sulfidation treatment, the bimetallic catalyst presents an average platinum–sulfur coordination number of 2 at a distance of 2.32 Å and no significant effect on the metallic bonding is measured. The platinum–metal coordination is 4.2 at a distance of 2.71 Å. Finally,

after the second reduction in flowing H<sub>2</sub> at 723 K, the environment of platinum atoms is composed of one sulfur atom at 2.30 Å and 4 platinum atoms at 2.71 Å.

Error analysis to check  $N$ ,  $\sigma$  correlation was again performed. Artificially constraining the Debye–Waller factors to constant values produced less satisfying fits to data and variations at the most of 10% in the Pt–S and Pt–M coordination numbers. These variations are too small to account for the decrease in Pt–S coordination from 2 to 1 after the second reduction.

The normalized EXAFS functions obtained at the rhodium L<sub>III</sub> edge for the PtRe catalyst after the different treatments are presented in Fig. 3(A) and

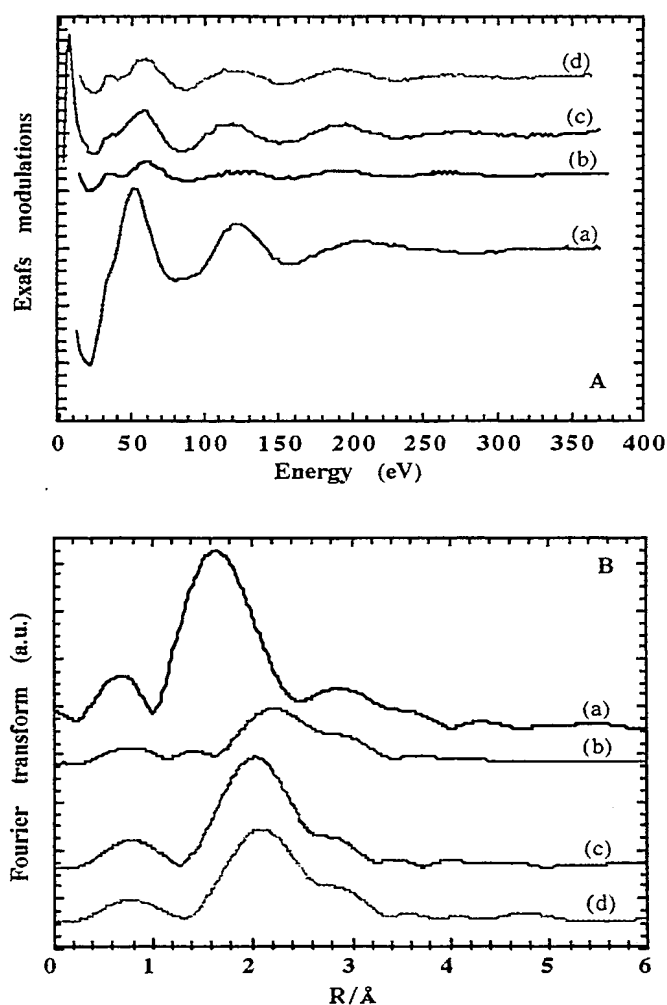


Fig. 2. EXAFS data at platinum  $L_{III}$  edge (A) and corresponding Fourier transforms (B) for the Pt/ $Al_2O_3$ -Cl sample collected during the following (a)–(d) (see Fig. 1).

the Fourier transforms are shown in Fig. 3(B). As for the preceding monometallic case, an inverse Fourier transform was then applied to give the rhenium EXAFS function which was then fitted using the appropriate references and the results are included in Table 3(b). The rhenium is not reduced completely to the metallic state. After reduction at 723 K, we measure an average rhenium–oxygen coordination number of 0.9 at a distance of 2.10 Å and 3.7 metal atoms at 2.68 Å. Similar results have been obtained by other authors [15,16]. After sulfidation in flowing 1%

$H_2S$  in  $H_2$  at 723 K, the rhenium local environment is composed of 4.5 metal neighbors at 2.74 Å and 2.4 sulfur atoms at 2.36 Å. Finally, after the second reduction in flowing  $H_2$  at 723 K, the environment of rhenium is composed of 2 atoms of sulfur at 2.34 Å and 4.7 metal atoms at 2.74 Å.

Theoretical backscattering amplitude calculations showed that the error induced by use of the same amplitude and phase parameters for Re–O distances as different as 1.76 and 2.1 Å is less than 10% of the oxygen coordination number.

Table 3

Numerical results of the analysis of Pt Re/Al<sub>2</sub>O<sub>3</sub>

	Number of atoms	Distances (Å)	Debye-Waller factor (Å)
<i>(a) Beyond the L<sub>III</sub> platinum edge</i>			
Initial catalyst	N <sub>O</sub> =6.2	R <sub>Pt-O</sub> =2.06	Δσ <sub>Pt-O</sub> =0.01
First reduction H <sub>2</sub> , 723 K	N <sub>O</sub> =0.3	R <sub>Pt-O</sub> =1.98	Δσ <sub>Pt-O</sub> =0.00
	N <sub>M</sub> =3.9	R <sub>Pt-M</sub> =2.71	Δσ <sub>Pt-M</sub> =0.03
Sulfidation 1% H <sub>2</sub> S/H <sub>2</sub> , 723 K	N <sub>S</sub> =2.0	R <sub>Pt-S</sub> =2.32	Δσ <sub>Pt-S</sub> =0.06
	N <sub>M</sub> =4.2	R <sub>Pt-M</sub> =2.71	Δσ <sub>Pt-M</sub> =0.06
Second reduction H <sub>2</sub> , 723 K	N <sub>S</sub> =1.0	R <sub>Pt-S</sub> =2.31	Δσ <sub>Pt-S</sub> =0.04
	N <sub>M</sub> =4.0	R <sub>Pt-M</sub> =2.72	Δσ <sub>Pt-M</sub> =0.02
<i>(b) Beyond the L<sub>III</sub> rhenium edge</i>			
Initial catalyst	N <sub>O</sub> =4.1	R <sub>Re-O</sub> =1.76	Δσ <sub>Re-O</sub> =0.00
First reduction H <sub>2</sub> , 723 K	N <sub>O</sub> =0.9	R <sub>Re-O</sub> =2.10	Δσ <sub>Re-O</sub> =0.08
	N <sub>M</sub> =3.7	R <sub>Re-M</sub> =2.68	Δσ <sub>Re-M</sub> =0.00
Sulfidation 1% H <sub>2</sub> S/H <sub>2</sub> , 723 K	N <sub>S</sub> =2.4	R <sub>Re-S</sub> =2.36	Δσ <sub>Re-S</sub> =0.00
	N <sub>M</sub> =4.5	R <sub>Re-M</sub> =2.74	Δσ <sub>Re-M</sub> =0.00
Second reduction H <sub>2</sub> , 723 K	N <sub>S</sub> =2.0	R <sub>Re-S</sub> =2.34	Δσ <sub>Re-S</sub> =0.00
	N <sub>M</sub> =4.7	R <sub>Re-M</sub> =2.74	Δσ <sub>Re-M</sub> =0.00

Table 4

Numerical results of the analysis of non-chlorinated Pt-Re/γ-Al<sub>2</sub>O<sub>3</sub>

	Number of atoms	Distances (Å)	Debye-Waller factor (Å)
<i>(a) Beyond the L<sub>III</sub> platinum edge</i>			
Initial catalyst	N <sub>O</sub> =6.5	R <sub>Ri-O</sub> =2.05	Δσ <sub>Pt-O</sub> =0.00
First reduction H <sub>2</sub> , 723 K	N <sub>O</sub> =0.3	R <sub>Ri-O</sub> =1.90	Δσ <sub>Pt-O</sub> =0.01
	N <sub>M</sub> =4.2	R <sub>Pt-M</sub> =2.70	Δσ <sub>Pt-Pt</sub> =0.04
Sulfidation 1% H <sub>2</sub> S/H <sub>2</sub> , 723 K	N <sub>S</sub> =2.1	R <sub>Pt-S</sub> =2.31	Δσ <sub>Pt-S</sub> =0.04
	N <sub>M</sub> =4.0	R <sub>Pt-M</sub> =2.71	Δσ <sub>Pt-M</sub> =0.08
Second reduction H <sub>2</sub> , 723 K	N <sub>S</sub> =1.0	R <sub>Pt-S</sub> =2.31	Δσ <sub>Pt-S</sub> =0.00
	N <sub>M</sub> =4.0	R <sub>Pt-M</sub> =2.71	Δσ <sub>Pt-M</sub> =0.06
<i>(b) Beyond the L<sub>III</sub> rhenium edge</i>			
Initial catalyst	N <sub>O</sub> =4.0	R <sub>Re-O</sub> =1.77	Δσ <sub>Re-O</sub> =0.00
First reduction H <sub>2</sub> , 723 K	N <sub>O</sub> =0.9	R <sub>Re-O</sub> =2.09	Δσ <sub>Re-O</sub> =0.08
	N <sub>M</sub> =3.4	R <sub>Re-M</sub> =2.68	Δσ <sub>Re-M</sub> =0.03
Sulfidation 1% H <sub>2</sub> S/H <sub>2</sub> , 723 K	N <sub>S</sub> =2.1	R <sub>Re-S</sub> =2.34	Δσ <sub>Re-S</sub> =0.00
	N <sub>M</sub> =3.9	R <sub>Re-M</sub> =2.72	Δσ <sub>Re-M</sub> =0.00
Second reduction H <sub>2</sub> , 723 K	N <sub>S</sub> =2.1	R <sub>Re-S</sub> =2.34	Δσ <sub>Re-S</sub> =0.00
	N <sub>M</sub> =4.2	R <sub>Re-M</sub> =2.71	Δσ <sub>Re-M</sub> =0.00

### 3.3. Non-chlorinated bimetallic Pt-Re/γ-Al<sub>2</sub>O<sub>3</sub> catalyst

In order to determine the effect of chlorine on the sulfidation process, the dechlorinated bimetallic sample was studied. Results are given in Table 4. As in the preceding case, the environment of the two metals in

the calcined state is composed essentially of oxygen, six for the platinum and four for the rhenium. The reduction process introduces a metal (either platinum or rhenium) in the local order around the two metals. Metallic clusters are thus generated, containing very few atoms as can be seen from the low metal coordination numbers. Contact with H<sub>2</sub>S does not change

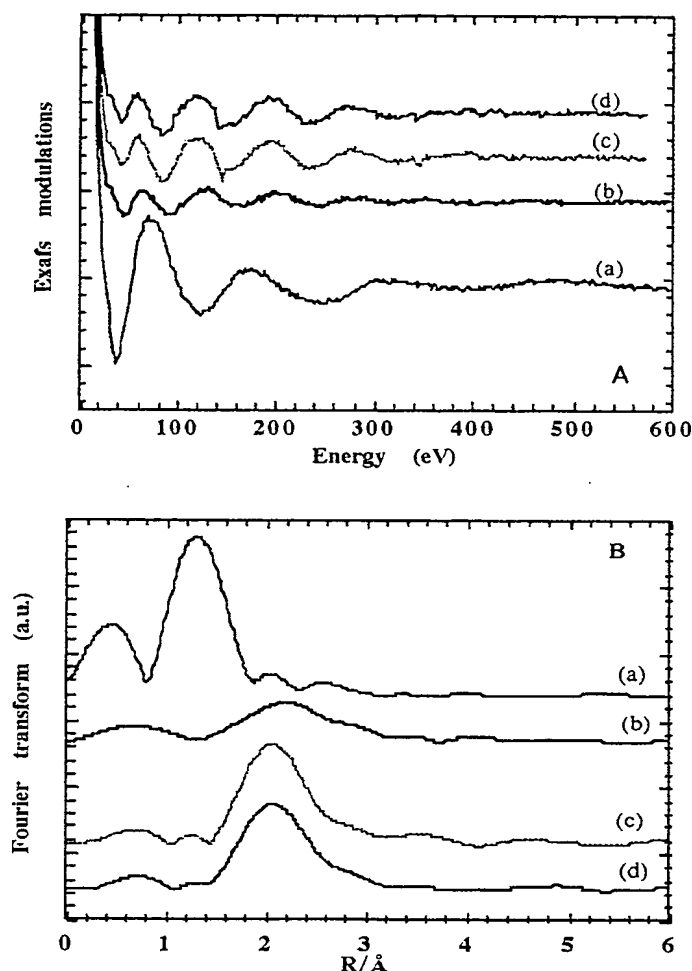


Fig. 3. EXAFS data at platinum L<sub>III</sub> edge (A) and corresponding Fourier transforms (B) for the PtRe/Al<sub>2</sub>O<sub>3</sub>-Cl sample collected during the treatments (a)–(d) (see Fig. 1).

the structural characteristics of the metallic clusters, the metal coordination numbers remaining the same. Sulfur atoms are located around both metals, quantitative simulations of the EXAFS modulations giving two sulfur atoms around each platinum and rhenium atom. If the catalyst is then submitted to pure hydrogen, part of the sulfur in the vicinity of the platinum is removed, the rhenium keeping its sulfur environment. Here again, variations in the Debye–Waller factor are too small to explain the change in Pt–S coordination after the second reduction.

Fig. 4 is an example of the high quality of agreement between the experimental and calculated spectra.

#### 4. Discussion

It is clear from EXAFS data that reduction under hydrogen produces in all three cases metallic particles of small dimensions. Metal–metal first shell coordination numbers of 4–5 indicate, on the basis of fcc structure, particle diameters of the order of 1 nm

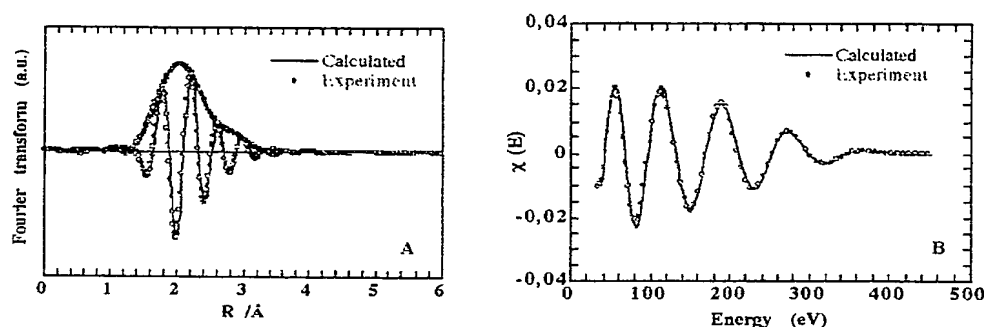


Fig. 4. Comparison at  $L_{III}$  rhenium edge of the imaginary and absolute  $k^3$ -weighted Fourier transform with the Hanning window from 40 to 500 eV, for the experimental spectrum ( $\circ \circ \circ$ ) and theoretical spectrum (solid lines) for the  $PtRe/Al_2O_3-Cl$  sample after the sulfidation treatment, in  $R$  space (A) and  $E$  space (B).

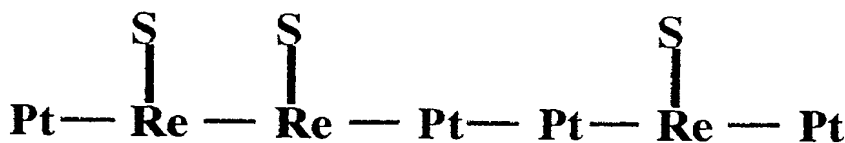


Fig. 5. Biloen's model.

[17]. Transmission electron microscopy studies of reduced catalysts confirmed that the particles were less than 0.7 nm in diameter (this value representing the detection limit for particles on transition aluminas).

Enhanced stability is the most spectacular advantage of the bimetallic  $PtRe$  system in comparison with the monometallic one. The positive effect of rhenium addition is only found when the catalysts are presulfided. To explain the superior activity maintenance of the  $PtRe$  a model schematically represented in Fig. 5 was proposed first in 1980 by Biloen et al. [18] and was further elaborated by Sachtler [19]. This model assumed that in the steady state the catalyst contains  $PtRe$  clusters on the alumina, and sulfur atoms are preferentially adsorbed on  $Re$  atoms at the surface of these clusters [4,5].

Recently, Bickle et al. [20] studied the effect of sulfur on the  $PtRe/Al_2O_3$  system during the reforming reaction. Using the results of catalytic tests of cyclohexane and  $n$ -heptane reforming, they proposed a model for sulfided  $PtRe/Al_2O_3$  inspired by that of Biloen et al. [10]. In this model, the sulfur is preferentially adsorbed onto the rhenium forming  $Re-S$  bonds up to saturation of the rhenium surface.

Subsequent sulfur adsorption onto platinum atoms creates first irreversible  $Pt-S$  bonds up to saturation and then reversible  $Pt-S$  bonds.

Bickle et al. [20] also showed that the sulfided bimetallic is the better catalyst for industrial use both from the point of view of selectivity towards isomer formation and for its coke resistance. Various authors have studied the effect of sulfur on the deactivation of  $Pt/Al_2O_3$  and  $PtRe/Al_2O_3$  [5,21–23]. They have shown that sulfur enhances the stability against deactivation of reforming catalysts and that this beneficial effect is greater for  $PtRe/Al_2O_3$  than for  $Pt/Al_2O_3$ . These results give supporting evidence for the above model. The above models were all based on catalytic activity results and no direct structural evidence has been given for the existence and reversibility of the sulfur-rhenium and sulfur-platinum bonds. The credibility of such models reposes on interpretation of indirect evidence and must therefore remain debateable in the absence of direct structural confirmation.

In order to confront such a model with direct structural evidence and to further discuss the way in which sulfur atoms are linked to platinum atoms, the sulfur content of the final catalyst has been checked. We find that there is globally one sulfur atom per



platinum atom. By EXAFS spectroscopy, we find in the vicinity of platinum atoms 2.8 sulfur atoms, indicating that sulfur atoms are bonded to at least two metal atoms, a result in line with previous ones [24]. One key point of this part of the study is the fact that sulfur modifies completely the structure of the platinum cluster. This was pointed out before in the case of large clusters of platinum and Harris and Tsang [25] have shown that sulfur induced faceting. Here, for very small platinum cluster, it seems that the platinum cluster is destroyed since no platinum–platinum bonds are found.

These results obtained on the monometallic platinum help us to understand the role played by the second metal. The fact that platinum–metal bonds still exist after the sulfidation underlines the role played by the rhenium atoms. As has been shown by several works already published [4,5,22,26,27], the presence of the second metal stabilizes the metallic cluster.

Thus, the basic metal structure is preserved in the bimetallic case but we clearly detect different affinities of the two metals for sulfur bonding. After sulfidation both rhenium and platinum atoms are coordinated to about two sulfur atoms. On the second reduction, the rhenium environment remains essentially unchanged, the adsorbed sulfur appearing irreversible under the conditions used. The sulfur bonded to platinum in the bimetallic system appears less stable, the coordination number falling by one half. The study of the dechlorinated bimetallic catalyst shows that chlorine plays no direct structural role in the stability of the particle during sulfiding and also supports the interpretation of the data for the PtRe/Al<sub>2</sub>O<sub>3</sub> system where the possibility of Pt–Cl and Re–Cl is not taken into account.

## 5. Conclusion

Our study of the sulfiding of Pt and PtRe systems adds new perspectives both for limiting the range of possible model systems and for a quantitative approach to the models. The lower catalytic activity of the monometallic system can be clearly related to the total disappearance of the metallic phase under the conditions of treatment used here. The sulfiding produces on the contrary almost no rearrangement of the metallic phase in either of the bimetallic systems

studied showing that in those cases the metallic sites are still available.

In addition, the results show clearly that the concept of selective poisoning of rhenium sites is correct, the sulfur bond to rhenium shows a much greater stability than that to platinum. Under the conditions used here for the second reduction, approximately half of the sulfur bonds to platinum are removed whilst the environment of rhenium remains unchanged. Thus, the notion of reversible and irreversible Pt–S bonds can also be quantified. The chlorine plays no direct role in the structural stabilization of the metal particles, as shown by the destruction of aggregates in the Pt/Al<sub>2</sub>O<sub>3</sub>–Cl system and the similarity of results for the two bimetallics. Improved catalytic performances of the chlorinated solids must therefore rather be due to synergy of the reactions facilitated by the metal and the acidic functions.

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